

Why Does Ga Addition to CIS Limit Its Cell Performance: The Amazing Physics of Grain-Boundaries and Killer-Defects in Chalcopyrites

A. Zunger

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Alex Zunger

National Renewable Energy Laboratory, Golden, Colorado, alex_zunger@nrel.gov

ABSTRACT

New theoretical studies reveal the way that grain boundaries lead to a reduction in electron-hole recombination in CIS, and how Ga addition leads to cell deterioration largely because of grain-interior (not boundary) effects.

Objectives, Technical Approach & Results

Whereas the *polycrystalline* form of conventional semiconductors (Si, GaAs) have poor transport and electronic properties relative to their crystalline counterparts, surprisingly, poly-crystalline alloys of CuInSe_2 (CIS; $E_g \approx 1.0$ eV) with CuGaSe_2 (CGS; $E_g \approx 1.7$ eV) has excellent properties, manifested, among others by nearly 20% solar cell conversion efficiency, outperforming even its crystalline counterpart.¹ In such chalcopyrite semiconductors the Group-I and III cations replace the two identical Group-II cations of zincblende $2\text{ZnSe} \equiv \text{Zn}_2\text{Se}_2$, adding more than 30% Ga deteriorates performance. This intriguing property of grain boundaries (GBs) in chalcopyrites has recently attracted much attention both because of its relevance to solar cell performance and, more generally, because of the hope that understanding the underlying mechanism at play in polycrystalline chalcopyrites might help design benign GB's in conventional polycrystalline semiconductors (e.g. Si and GaAs) to the benefit of low-cost devices.

We have explained theoretically¹ why, despite the existence of many defects and impurities at the GBs of CuInSe_2 , there appears to be negligible recombination of electrons and holes there. Our conclusion is based on the analogy between the structure of GB "internal surfaces" and the surface structure of CIS films. Total-energy minimization of the surface structure of CIS² showed that in contrast with conventional semiconductors such as GaAs, in CIS the polar surface is more stable than the non-polar surface. Like in GaAs, polar CIS surfaces must reconstruct to remove the electrostatic dipole created by the alternation of pure cation and pure anion planes along the polar axis. This reconstruction involves creating rows of either Cu vacancies [in the metal-exposed (112) surface] or In-on-Cu antisites [at the subsurface of the anion-exposed ($\bar{1}\bar{1}\bar{2}$) face]. Unlike conventional bulk vacancies, this surface Cu vacancy is charge-neutral because its negative (acceptor-like) charge has been used to cancel the electrostatic dipole. Furthermore, unlike GaAs, this reconstruction

in CIS costs little energy because the creation of vacancies in the weakly bonded Cu sublattice is less costly than the creation of Ga vacancies in the strongly covalently bonded III-V's. Thus, the interface between GB and grain interior (GI) represents an interface between two materials of different chemical compositions – one strongly Cu poor and one more closely Cu stoichiometric. This leads to a band offset between the GB and GI involving a (112) lowering of the valence band maximum (VBM) at the Cu-poor GB [Fig 1(a)]. The calculated GB/GI conduction band offset ΔE_c in pure CIS was negligible. The reason that the Cu-poor material has a lower VBM is that it is deprived of Cu *d* orbitals, which when present, repel the Se *p* based VBM upwards.³

The predicted existence of a low VBM on the GB side causes photogenerated holes to be repelled from the GB into the GI. Although, the GB has numerous defect recombination centers, the electrons there have no holes to recombine with. At the same time, recombination in the GI of solar cell quality CIGS is rather weak, as most impurities and defects have migrated during growth into the GB, leaving the GI potentially more perfect and pristine than conventional single-crystal CIS. This model¹ of *charge-neutral* hole reflector at the GB due to a compositional band offset is a new concept, which differs from the conventional model of *charged* GB's. In the latter model, offered originally for Si⁴ and adopted later for II-VI's and chalcopyrites,⁵ one assumes that the GB has a net concentration of a charged donors, which causes a downward bending of *both* valence and conduction bands. Recent detailed modeling⁶ has shown, however, that even though positive (donor) electrostatic charges at the GB will repel holes, they will attract electrons sufficiently to raise the electron-hole *n-p* product, thus leading to enhanced recombination and reduced solar cell efficiency. Although charged defects and impurities may exist at the GB these do not improve cell efficiencies as previously hoped.⁵

Our model of GB/GI charge-neutral band offset hole reflector was recently studied experimentally^{7,8} and via device simulations.⁶ Micro Auger electron spectroscopy measurements⁷ found a large (up to 50%) deficiency of Cu at the CIS grain-boundary, as predicted by the polar surface reconstruction model.¹ Pump-power dependent Cathodoluminescence (CL) studies⁸ showed strongly reduced recombination at the GB and rapid saturation of the CL energy with power

at the GB, indicating the limited supply of one type of carrier there. Scanning Tunneling Microscopy (STM) scans at low voltage, (when only electrons are injected from the tip into the GB) revealed⁹ a decrease in photon emission intensity at the GB when compared to GI, demonstrating a reduced hole density at the GB as predicted by the model. Two dimensional device simulations of the model of neutral offset at the GB/GI interface indicate a strongly reduced recombination at the GB (on account of a reduced $n \cdot p$ product), leading to a significant increase in solar cell efficiency relative to a cell having no band offset at the GB/GI interface.

Figure 1 shows further that: (i) anion-terminated GB's have negligible ΔE_v in CIS and CGS; (ii) cation-terminated CGS has a larger GB ΔE_v compared to CIS; (iii) the cation-terminated CGS has a large GB ΔE_c than CIS; (iv) relative cell performance of CIS vs. CGS: Three factors are pertinent here: (a) we have shown¹⁰ that an important reason for the lesser performance of Ga-rich (more than 30% Ga) CIGS solar cells is due to different behaviors of their GI not GB. Both materials exhibit pinning of the Fermi level

at about $E_v + 0.8$ eV due to the spontaneous formation of electron-annihilating V_{Cu} acceptors; however this energetic position is 0.9 eV below the CBM of CGS, whereas it is only 0.2 eV or less below the CBM of CIS. Thus, the maximum attainable voltage is more limited in Ga-rich material; (b) At abrupt GI/GB interfaces, the carrier transport can be limited by tunneling assisted electron-hole recombinations (as in conventional charged pn -junctions⁴). Whereas in CIS the energy difference $\Delta_g = E_c(GB) - E_v(GI)$ at the charge-neutral GB/GI interface (Fig. 1) nearly equals the bulk CIS band gap, in CGS the smaller $\Delta_g = 0.6$ eV at the (112) GB/GI interface will increase recombination; (c) The larger ΔE_c in CGS can affect V_{oc} : In the space charge region near the CdS/CIGS interface, the band profile restricts V_{oc} and thus the cell performance. In CIS $\Delta E_c = 0$ (Fig. 1) which does not limit V_{oc} . However, in CGS the strong downward band bending ΔE_c at the GB will affect V_{oc} adversely. Effects (a) – (c) lead to a lesser performance of CGS relative to CIS.

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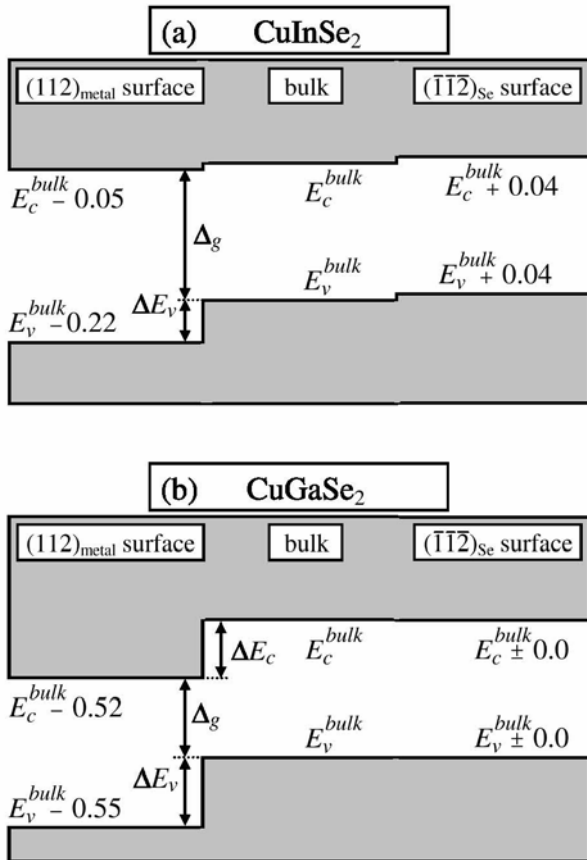


Fig. 1. Band offset energies (in units of eV) of (112) cation metal and (112) anion Se terminated surfaces of CIS and CGS. The error bar is estimated to 0.05 – 0.10 eV.

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